NASA TT F-10,921

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Translation of "Vivchennya vplivu riznikh travnikiv i
leguvannya poverkhni na fotoprovidnost'
monokristaliv sul'fidu kadmiyu"
Ukrains'kyy Fizichnyy Zhurnal,
No. 4, pp. 453-455, 1966

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546 MAY 1967

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STUDY OF THE EFFECT OF VARIOUS PICKLING AGENTS AND SURFACE ALLOYING ON THE PHOTOCONDUCTIVITY OF CADMIUM SULFIDE SINGLE CRYSTALS

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ABSTRACT. It has been established that the photosensitivity of CdS crystal surfaces is not materially affected by the type of pickling agent. Some success is anticipated in the development of so-called polishing pickling substances designed to produce a mirror-like surface on the crystal. The effect of various admixtures in the CdS crystal surfaces on the spectral distribution of their photoconductivity is outlined in graphic form.

The chemical pickling agents used to detect dislocations in CdS single crystals are described in refs. 1-5. However, there is no information on the polishing substances for CdS required in connection with a number of physical investigations. Information on the effect of pickling substances and their impurities on the photosentivity of CdS crystals is unavailable also, but the powerful effect of surface characteristics on the photosensitivity of CdS (ref. 6) makes these problems quite urgent. /453*

The purpose of this study was 1) to find polishing pickling substances for CdS; 2) to study the effect of pickling agents on the photosentivity of CdS; 3) to study the effect of certain admixtures introduced into the surface layer of CdS in the pickling process on the spectral distribution of the photoconductivity.

Fine unalloyed and mirror-surfaced CdS single crystals grown from a vapor phase by the Frerichs method were investigated. A structural X-ray analysis revealed that the (1120) plane was the pickling plane.

The CdS single crystals were pickled in a platinum cup, washed with a double distillate, rinsed with alcohol and then dried at 60-70°C. Sone of the crystals were degreased in CCl_4 before pickling. "CP" (chemically pure) agents were used to prepare the pickling substances. The surface quality of the specimens was checked after the pickling under an MIM-7 microscope. The Au, Cu and Sb admixtures were included in the CdS surface from the pickling substances which contained the salts of these metals in various concentrations. The photosensitivity of the CdS single crystals was investigated in a device similar to the one described in reference 7. The possiblity was provided in it for measuring the proper lifetime τ and the phenomenological quantum yield G_f by the method indicated in reference 8.

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* Numbers in the margin indicate pagination in the original foreign text.

A total of almost 25 pickling agents was studied. The chemical composition and pickling conditions of the 12 best studied substances are listed in the table which also indicates the quality of the surface after the pickling. The pickling agents 1-5, described in literature, produce a dull surface, and agents 6, 7, 9 and 12 a polished surface.

Pickler No.	Composition of Pickler	Pickling Time	Pickling temp. °C	Surface appearance after pickling	Refs.
1	6M HCl	1 min	25	dull	6
2	$1HCl+1HNO_3+1H_2O$	20 sec	25	dull	1
3	$0.5M\ K_2Cr_2O_7X15N\ H_2SO_4$	20 sec	95	dull	1
4	$6\ CH_3COOH+6HNO_3+1H_2O$	20 sec	25	dull	3
5	1 HCl+3 thiourea (100 g/l)	20 sec	60	dull	5
6	HPO_3	10 sec	boiling	polished	
7	$KJ+C_6H_8O_7H_2O$ solution	15 sec-2 min	90	polished	
8	$KJ+C_4H_6O_6$	5 min	160-170	dull	
9	$KBr+C_6H_8O_7$	5 min	160-170	polished	
10	$KJ+C_6H_8O_7H_2O$ smelting	3 min	150-160	polished	
11	benzene	1 min	boiling	polished	
12	toluene	1 min	boiling	polished	

It has been established that most of the pickling substances do not materially change the photosensitivity of CdS crystal in white light. And the change of photosensitivity that was observed in some cases disappeared in time (several days). For example, the use of pickling agents 7 and 10 resulted, as a rule, in an increasedphotosensitivity (up to 50 percent). But this increase was not observed two weeks later--if the crystal was kept in the air.

It is possible that the CdS surface characteristics are brought about primarily by the effect of the stable layer of adsorbed molecules on the crystal surface. A certain length of time is required in this connection to remove the volatile components of the pickling substance which remain on the surface despite the thorough washing. From this point of view the insignificant role of the chemical composition of the pickler and the lack of change in the photosensitivity after the pickling become understandable.

Some effect of the pickling on the spectral characteristics of the photocurrent was noted. Thus the use of the widespread pickler 1 reveals a decreasing photosensitivity in the shortwave region of the spectrum, and the employment of pickler 2 reduces the photosensitivity in the shortwave region, and of its maximum level, and there is some increase of sensitivity in the longwave region which is explained by the effect of the pickling on the effectiveness of the surface recombination centers.

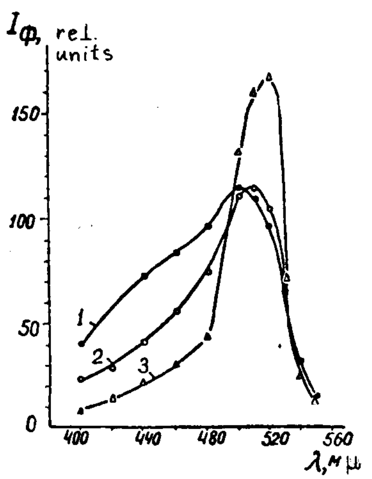

Figure 1. The spectral dependence of the photoconductivity of a CdS crystal on a surface alloyed with Au:

1- before pickling, 2- after pickling in 6M HCI, 3-after alloying with Au.

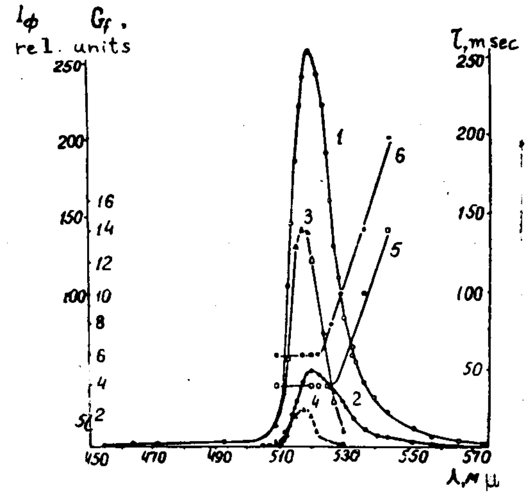

Figure 2. The spectral relationship of photoconductivity I phenomenological quantum yield G_f and proper lifetime

1,2-$I_\Phi(\lambda)$; 3,4-$G_f(\lambda)$; 5,6-$\tau(\lambda)$;

1,3, 5-CdS; 2,4, 6-CdS with Cu-alloyed surface.

It is obvious that the polishing picklers 7.9 – 12 which can be used to produce a mirror-like surface hold out some promise in the field of physical investigations. Metallic admixtures were added to the surface from picklers 1, 2 and 4. The spectral distribution of the photoconductivity of the CdS crystal is shown in figure 1. It appears from figure 1 that the photosenstivity in the shortwave region of the spectrum declines as a result of alloying Au with the surface, which may be due to the appearance of new recombination centers. An increase of photosentivity (two- and threefold) was noted in the highest photocurrent region in most cases. Measurements of the phenomenological quantum yields revealed that it also increases in this region of the spectrum, and the photosensitivity change in the maximum region is always accompanied by a similar change of the quantum yield.

In some cases the alloying of the CdS surface with Sb resulted in a slightly higher photosensitivity in this region of the spectrum.

The introduction of a Cu admixture (fig. 2), just like Au, is conducive to a lower photosensitivity in the shortwave region but, unlike Au, the sensitivity in the maximum photocurrent region is reduced. It was found that in this case the phenomenological yield of photocurrent is also considerably reduced even though the proper lifetime is slightly increased.

If the declining photosensitivity in the shortwave region of the spectrum can be associated with the new combination centers and the strengthening of the recombination s-channel (ref. 8) produced by the alloying operation, the change of the photosensitivity in the maximum photocurrent region is possibly associated with the changing curvature of the surface zones and the rapidity of the recombination processes (for example, in the r-channel (ref. 8)) in the spatial charge layer.

In conclusion, we consider it our duty to express our sincere gratitude to V. A. Tyagay, candidate of chemical sciences, M. K. Sheynkman, candidate of physico-mathematical sciences, and G. I. Golynniy for their participation and discussion of the results.

Bibliography

1. Reynolds, D. C. and Czysak, S. J. Journal of Applied Physics, 31, 94, 1960.
2. Wolff, G. A., Frawley, J. J. and Hietanen, J. R. Journal of the Electrochemical Society, 111, No. 1, 22, 1960.
3. Warekois, E. P., Lavine, M. C., Mariano, A. N. and Gatos, H. C. Journal of Applied Physics, 33, No. 2, 690, 1962.
4. Bakradze, R. V., and Rom-Krichevskaya, I. A. Kristallografiya (Crystallography), 8, Second Edition, 238, 1963.
5. Holmes, P. J. "Electrochemistry in Semiconductors," N. Y., 1962.
6. Bube, R. H. Physical Review, 83, 393, 1952; Journal of Chemical Physics, 27, 496, 1957; Ryvkin, S. M. and Khansevarov, R. Yu. Zhurnal Tekhnicheskoy Fiziki, 27, 925, 1958. Sal'kov, Ye. A., Fedorus, G. A. and Shenkman, M. K. Fizika Tverdago Tela, 1, 579, 1959.
7. Kinev, St., Sheynkman, M. K., Shul'ga, I. B. and Fursenko, V. D. Pribory i Tekhnika Eksperimenta. No. 2, 154, 1962.
8. Lashkarev, V. Ye., Sal'kov, Ye. A., Fedorus, G. A. and Sheynkman, M. K. Reports of the USSR Academy of Sciences (DAN SSSR), 114, 1203, 1957; Ukrainskyy Fizychnyy Zhurnal, 2, 261, 1957.
9. Lashkarev, V. Ye. Fizika Tverdago Tela, 5, 426, 1963; Lashkarev, V. Ye., Golynnaya, G. I. and Sheynkman, M. K. Fizika Tverdago Tela, 5, 3420, 1963.

Translated for the National Aeronautics and Space Administration
by John F. Holman Co. Inc.
WASHINGTON, D.C. 20037
NASw-1495